

First excited states of *p*-(*N,N*-dimethylamino)benzonitrile: a molecular orbital analysis

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Abstract

Following the molecular orbitals of *p*-(*N,N*-dimethylamino)benzonitrile (DMABN) along the most important reaction pathway from the $\pi^* \leftarrow \pi$ transition to the locally excited (LE) state and from there to the twisted intramolecular charge transfer (TICT) state, we gain substantial insight into the mechanism of the TICT phenomenon. In the ground state geometry the π^* orbital centred on the cyano group is too high in energy to be directly attainable in the $S_1 \leftarrow S_0$ Franck–Condon (FC) excitation. As the FC geometry relaxes by stretching the $C \equiv N$ bond the energy of this orbital decreases rapidly. As a result its contribution to the developing LE state becomes important. Starting from the LE state, torsion of the dialkylamino group causes a change in the character of the ground state highest occupied molecular orbital (HOMO) from π to an amino-group-centred, in-plane orbital which means that a TICT state has been formed. The resulting TICT emission probability is consistent with the experimentally observed thermal activation of the emission rate.

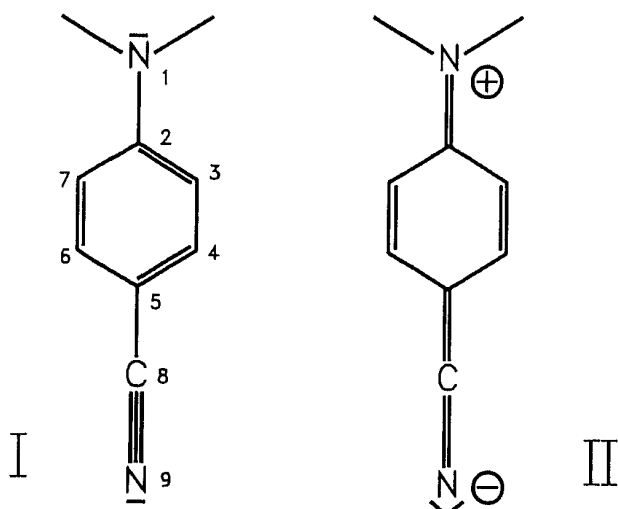
1. Introduction

The phenomenon of the dual fluorescence of *p*-(*N,N*-dimethylamino)benzonitrile (DMABN) and structurally related compounds in polar solvents has given rise to scientific controversy over its origin which has been going on for the last four decades [1, 2]. Quantum chemical calculations at different levels of approximation have been carried out to clarify the experimentally supported notion of high-polarity, twisted intramolecular charge transfer (TICT) states [3, 4]. While Majumdar *et al.* [2] stress the relevance of full ground state geometry optimization in their recent computational study on DMABN, little attention has yet been paid to the effect of changes in structural parameters other than the amino group torsional angle on the nature and energy of the lowest lying excited states.

However, by studying the resonance formulae [5] I and II of DMABN, we might argue that II represents a more appropriate description of a molecular charge transfer (CT) state than I. Following this argument, we expect a lengthening of the C_8-N_9 bond and a concomitant shortening of the N_1-C_2 and C_5-C_8 bonds in CT structure II relative to I. By analogy with benzonitrile, a low-lying π^* orbital centred on the cyano group is expected to act as a CT acceptor [6]. For this reason, structural

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variations, particularly in this substituent, leading to a potential stabilization of the cyano-group-centred antibonding π^* orbital, seem inherently interesting. The quinoid polar structure II can appear only in the planar form. It assumes a strong coupling of the amino group with the ring system. In the twisted form such a structure is excluded. Grabowski *et al.* [3] have reluctantly parted with their original hypothesis that, in DMABN, CT occurs between the lone pair of the $-\text{NMe}_2$ group and an in-plane π^* orbital of the $-\text{CN}$ group, due to contradiction from CNDO/S calculations which predict that the corresponding configuration interaction (CI) state lies about 4.5 eV above the first excited state [7]. Simulations of the TICT phenomenon not only demands extensive CI calculations, but also inclusion of solute-solvent interaction. While it is obvious from the simple Born equation [8] that the stability of a state with separated charges can only be described if the solvent properties are included, quantitative simulation of the TICT state is a very demanding task and is not the aim of this short paper. However, by accepting the experimental fact and the qualitative theoretical understanding that some minimum solvent polarity is needed to stabilize the charges of the TICT state, we can gain substantial insight into the mechanism of the TICT phenomenon by following the molecular orbitals along the most important reaction pathway.



2. Experimental details

Calculations were carried out by the extended Hückel method [9], with the parameters collected in Table 1. Parameters were kept constant during all the calculations. Mulliken population analysis was applied [10] and the coulomb integrals H_{ii} were

TABLE 1

Extended Hückel molecular orbital parameters ($\kappa=1.0$; $\delta=0.35$)

Element	n	ζ_{ns}	H_{ss} (eV)	ζ_{np}	H_{pp} (eV)
H	1	1.300	-13.60		
C	2	1.71	-21.4		
N	2	2.14	-26.0	1.625	-11.4
O	2	2.575	-28.20	1.95	-13.4
				2.225	-12.40

taken from ref. 9 for the hydrocarbons. For oxygen they were obtained by charge iteration on H₂O and nitrogen at the equilibrium geometry with the parameters from ref. 11. The off-diagonal elements were calculated as [12]

$$H_{ij} = \frac{1}{2}KS_{ij}(H_{ii} + H_{jj}) \quad (1)$$

To approximate the Wolfsberg-Helmholz constant, we used the weighted formula [13] in its distance-dependent form [14]

$$K = 1 + \kappa e^{-\delta(R-d_0)} \quad (2)$$

To correct for the core-core repulsion, a two-body term, as explained in ref. 14, was taken into account.

To significant precision, the geometrical parameters given in Table 1 of ref. 2 were used for the planar structure I and structure II was approximated by the introduction of the above-mentioned >C-NR_2 , >C-CN and $\text{-C}\equiv\text{N}$ concerted bond length changes of 0.1 Å each.

3. Results

The analysis of our computational results demonstrates that a change in the >C-NR_2 and >C-CN bond lengths by a reasonable amount (about 0.1 Å) does not affect the excited state and ground state properties fundamentally. We therefore focus on the increase in the C₈-N₉ bond length and on the amino group torsional angle, since their effects dominate. Neglecting the other two coordinates does not have a qualitative impact on the conclusions drawn. We present the results within the C_{2v} point group; thus the *z* axis coincides with the twofold rotational axis C₂ and *x* lies in the plane of the aromatic ring. This allows a simplified discussion without losing important information.

Let us first note that, in organic molecules, the following three types of intramolecular electronic transitions can usually be distinguished: $\pi^* \leftarrow \pi$ in which the charge redistribution is often of minor importance, $\pi^* \leftarrow n$ in which charge transfer from a lone pair to a π system occurs and $\pi^*(A) \leftarrow \pi(D)$ in which an electron is transferred from a donor to an acceptor part of the molecule. The last possibility is referred to as a locally excited (LE) state. A TICT state emerges out of an LE state if the donor and acceptor parts twist with respect to each other so that an approximately orthogonal conformation results [2].

On the left side of Fig. 1 we start from the planar S₀ ground state of DMABN with the two first sets of $\pi^* \leftarrow \pi$ transitions. Set I represents the *x*-polarized $\pi^*(a_2) \leftarrow \pi(b_2)$ and $\pi^*(b_2) \leftarrow \pi(a_2)$ excitations, giving rise to the S₁ state of B₁ symmetry. Set II represents the *z*-polarized $\pi^*(b_2) \leftarrow \pi(b_2)$ and $\pi^*(a_2) \leftarrow \pi(a_2)$ excitations, giving rise to the S₂ state of A₁ symmetry [15]. CI treatment to create the desired transitions between electronic states, namely the *x*-allowed S₁(B₁) \leftarrow S₀(A₁) and the *z*-allowed S₂(A₁) \leftarrow S₀(A₁) transitions, would not be a difficult problem mathematically [16], but there is no way to circumvent appropriate parametrization. We therefore prefer to discuss the results on a one-electron basis which leads to an interesting pictorial interpretation.

In the ground state geometry on the left side of Fig. 1, $\pi_7^*(b_1)$ is too high in energy to be directly attainable in the S₁ \leftarrow S₀ Franck-Condon (FC) excitation. However, occupation of the C \equiv N antibonding π_5^* orbital in this transition causes weakening of the C \equiv N bond. As the S₁ FC geometry relaxes by stretching the C \equiv N bond, the energy of the b₁ symmetry in-plane orbital π_7^* decreases rapidly, by as much as 1.2 eV during stretching of 0.1 Å. Thus π_7^* becomes the superjacent lowest unoccupied

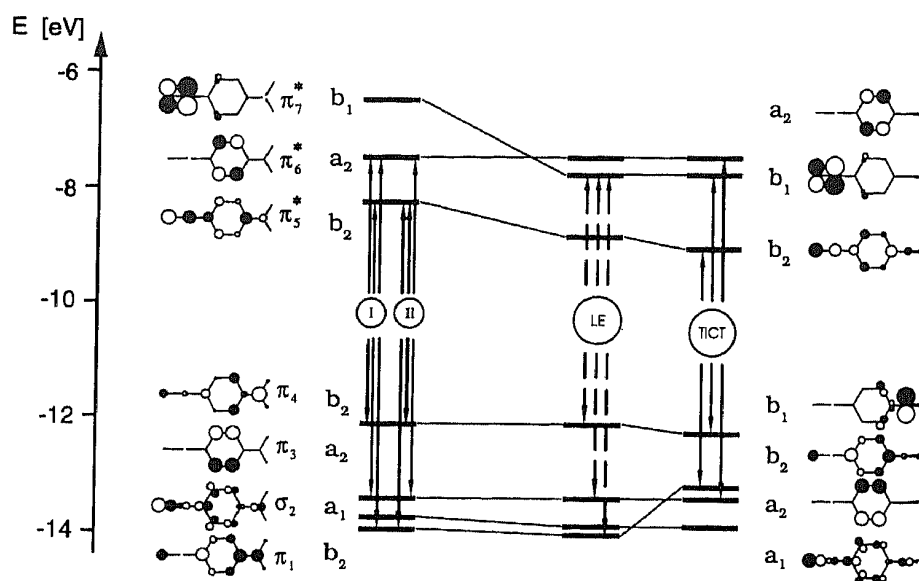


Fig. 1. Correlation diagram (frontier orbital region) for DMABN resulting from extended Hückel molecular orbital calculations. The values for the amino group torsional angle and the C≡N bond length are as follows: left: 0°, 1.16 Å; centre: 0°, 1.26 Å; right: 90°, 1.26 Å.

molecular orbital (LUMO). As a result its contribution to the developing partial CT state increases rapidly. The molecule ends up in the LE state indicated in Fig. 1 with broken arrows.

Starting from the LE state, we now consider torsion of the dialkylamino group 90° out of plane. The main event observed is that the $\pi_4(b_2)$ orbital changes in character to become an in-plane, amino-group-centred orbital of b_1 symmetry. The destabilization of the π_1 orbital should also be noted which influences the character of the highest occupied molecular orbital (HOMO) region. With increasing weight of the A_1 symmetry (b_1)¹(b_1)¹ configuration in the new state, which can be assigned as the TICT state, the charge separation becomes more complete. As already mentioned, stabilization of such a state is enhanced by solvent polarity.

The density of the low-energy excited configurations of A_1 symmetry increases, due to the large stabilization of the π_7^* orbital, the destabilization of the π_1 orbital and the change in character of the π_4 orbital, from left to right in Fig. 1. From a symmetry viewpoint a z -allowed transition to the ground state is possible. TICT emission has empirically been shown to be mainly long-axis (z) polarized and rather strong in intensity [17]. However, we must consider that the two b_1 orbitals emerging from $\pi_4(b_1)$ and $\pi_7^*(b_1)$ have nearly zero overlap. The (b_1)¹←(b_1)¹ transition probability in the ideal TICT geometry is therefore expected to be relatively low, but is not forbidden by symmetry. It can be enhanced if we move from the TICT state in the direction of the LE state, because then this transition probability increases according to the mechanism explained in a previous paper [18], where we described the change in the transition moment as a function of the amino group torsional angle of pyronine B. This observation is consistent with the experimentally observed thermal activation of the emission rates [1].

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